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CRYSTAL STRUCTURE AND INFORMATION THEORY

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I. *Introduction.*—From the standpoint of “information theory” as set forth by Shannon,¹ Shannon and Weaver,² Brillouin,³ and others and more particularly from the viewpoint of “description mechanics,”⁴ the study of crystal structures using X-ray data involves the consideration of three models. These models have a point-by-point relationship with one another as follows: (1) the crystal is called the “describee,” (2) the diffraction pattern is a “code” which is to be deciphered, and (3) the proposed structure (or solution) is a “replica” which should have a direct similarity to the describee.

The basic assumption in this type of study is that no more information can be gained than is contained in the diffraction pattern. The “descriptive capacity” of the crystal as a describee and of the diffraction pattern as a code can be computed, and thus the adequacy of the diffraction pattern in describing the crystal can be estimated. The methods for making such estimations will be illustrated in the following paragraphs through the use of a one-dimensional diffraction pattern.

II. *The Describee.*—Following the methods of description mechanics, we first draw a line whose length represents the length a of a single crystallographic unit cell in the x direction. Then we mark the distance a into N equal intervals which we call “description boxes.” These description boxes each have dimension $\Delta x = a/N$. This distance, Δx , represents the accuracy with which we wish to locate the atoms in the unit cell. If we know from other sources that there are M identical atoms per unit cell, then the descriptive capacity of the crystal is the number of ways of placing M atoms in N boxes with no more than one atom per box. If we were dealing with point atoms, the descriptive capacity ω_c' would be

$$\omega_c' = \frac{N!}{M!(N-M)!}, \quad (1)$$

But, since atoms occupy volumes that greatly exceed the limits of accuracy, another

more appropriate equation has been devised. Assuming that each atom occupies r boxes, the descriptive capacity ω_c is

$$\omega_c = \frac{r^{N/r}(N/r)!}{M!(N/r - M)!} = (d/\Delta x)^{a/d} \frac{(a/d)!}{M!(a/d - M)!} \quad (2)$$

where d is the diameter of an atom.

III. *The Code*.—The data from the diffraction pattern can describe the crystal structure, provided that the descriptive capacity of the diffraction pattern equals or exceeds that of the crystal. The diffraction pattern furnishes the Miller indices h and the absolute magnitudes of the amplitudes $|F_h|$ which represent the structure through the equation

$$\rho(x) = \frac{1}{V} \sum_h |F_h| \cos(2\pi hx - \alpha_h) + \frac{F_0}{V}, \quad (3)$$

where $\rho(x)$ is the electron density at the point x , V is the volume of the unit cell, and α_h is the phase angle of the diffracted wave. Usually, in practical work, the accuracy of measuring amplitudes cannot be expressed as a percentage; but the value $|F|_w$ assigned to the weakest visible maximum is the increment of inaccuracy for all maxima. Therefore, this increment could be called a "diffraction slug" and the number, S_h , of them in a diffraction spot is $S_h = |F_h|/|F|_w$. The total number in the entire diffraction pattern is

$$S = \sum_h \frac{|F_h|}{|F|_w}.$$

Fortunately, the diffraction pattern is by nature divided into "diffraction boxes" or distances in *reciprocal* space and the number of such boxes is simply H , the number of diffraction maxima or spots. If this problem were simply that of computing the number of ways of placing S slugs in H boxes without regard to the number per box, then the descriptive capacity ω_d''' of the diffraction pattern would be

$$\omega_d''' = \frac{(H + S - 1)!}{(H - 1)! S!}. \quad (4)$$

However, two additional things must be considered. The first of these is the phase angle which might be estimated by some means with an assumed accuracy of $2\pi/\eta$; and the number of ways of classifying H boxes into η classes is η^H . Thus ω_d''' should be altered to

$$\omega_d'' = \frac{\eta^H (H + S - 1)!}{(H - 1)! S!}. \quad (5)$$

The second correction that must be made is to take care of the fact that diffraction maxima cannot assume unlimited values, but each value is limited to $|F_h| \leq Mf_h$, where M is, as before, the number of atoms in the unit cell and f_h is the atomic scattering factor in the direction prescribed by h and the wave length λ . The values of f_h are readily available in published tables as a function of $(\sin \theta)/\lambda = h/2a$. Calling the maximum value of S_h , Q_h , a special alteration was derived for equation (4):

$$\omega_d' \doteq \left[\prod_{h=1}^{H-1} (Q_h + h) \right] \frac{1}{(H-1)!}, \quad (6)$$

and the first correction η^H still has to be applied. So the restricted descriptive capacity of the diffraction pattern is

$$\omega_d \doteq \eta^H \left[\prod_{h=1}^{H-1} (Q_h + h) \right] \frac{1}{(H-1)!}. \quad (7)$$

It is interesting to note that equation (7) reduces to equation (5) when the upper limits, Q_h , for S_h are all identical and as high as possible, i.e.,

$$Q_1 = Q_2 = \dots = Q_h = \dots = S.$$

IV. *Comparison of Describer and Code.*—If the diffraction data are adequate for determining the structure, then (see eqs. [2] and [7])

$$\omega_c \leq \omega_d$$

or

$$\frac{(d/\Delta x)^{a/d} [(a/d)!]}{M! (a/d - M)!} \leq \eta^H \left[\prod_{h=1}^{H-1} (Q_h + h) \right] \frac{1}{(H-1)!} \quad (8)$$

Equation (8) can be used for either one or two purposes: (a) to determine the accuracy of Δx in locating atoms,

$$\Delta x = \frac{d[(a/d)!]^{d/a}}{[\omega_d M! (a/d - M)!]^{d/a}}, \quad (9)$$

or (b) to determine how many phases; q , are yet to be estimated in order to attain a given accuracy Δx . This is done by replacing H by q in the η^H term of equation (8) and solving for q , thus:

$$\omega_c = \eta^q \omega_d$$

or

$$q = \ln (\omega_c / \omega_d) / \ln \eta.$$

V. *Past Efforts.*—The use of these tests on actual crystal structures and their X-ray data as reported in the literature confirms the belief that has been held by crystallographers for two decades, "the X-ray data oversolves the structure." This implies that there are relationships between the magnitudes of the F values that determine the phases. The Patterson⁵ method combined the $|F_{hkl}|^2$ values and the knowledge of atoms to derive a structure. The Harker-Kasper⁶ inequalities derived certain phase relationships strictly on the basis of the F values, while Wrinch,⁷ Buerger,⁸ McLachlan,⁹ Clastre and Gay,¹⁰ and the others who developed the methods of shifted Patterson maps demonstrated that certain symmetrical structures can be solved by using only the magnitudes of the F values, provided that one through-center interatomic vector can be established. Harker and McLachlan¹¹ showed the principles of phase determination implied by the methods of shifted Patterson products. The extensive work of Karle and Hauptman,^{12, 13} as well as the writings of Goedkoop,¹⁴ all confirm the same faith. Methods devised

by Sayre,¹⁵ Zachariasen,¹⁶ and others are further examples; and the use of simultaneous equations proposed by Robertson¹⁷ shows promise.

VI. *A Suggestion.*—To show that much can be learned about the signs of the F values from little data other than the magnitudes of F , we shall demonstrate a principle based on gambling. If a structure is symmetrical, only two values of α_h need be considered, 0 and 180° , so that

$$\rho(x) = \frac{2}{V} \sum_h \pm |F_h| \cos 2\pi hx + \frac{F_0}{V} \quad (10)$$

if the value of $\rho(0)$ were known, for example; then

$$\rho(0) = \frac{2}{V} \sum_h \pm |F_h| + \frac{F_0}{V}$$

or

$$\sum_h \pm |F_h| = \frac{V}{2} \rho(0) - \frac{F_0}{2}. \quad (11)$$

With the $|F_h|$ values known, there are limitations on the choice of the \pm signs which permit the sum to add up to the known value $(V/2)\rho(0) - F_0/2$. The worst possible case would be where all $|F_h|$ values were equal. This is analogous to a penny-tossing game in which F dollars are won when heads appear and F dollars are lost when tails appear. After H throws of the penny, the net gain or loss is determined by the prevalence of heads, H_H , or tails, H_T , where

$$H_H + H_T = H.$$

This is similar to the equation of a straight line shown in Figure 1,

$$x + y = a.$$

The number of kinds of sequences of heads and tails in H tosses is equal to the number of paths from the point 0 to the line HH , where only moves to the right and upward are permitted. This number is $\omega_p = 2^H$, while the number of ways of getting H_H heads and H_T tails is

$$\omega(H_H, H_T) = \frac{H!}{H_H! H_T!}. \quad (12)$$

These results are shown for $H = 7$ in Figure 1, and, since there are usually many ways of getting H_H heads and H_T tails, knowing the final score does not uniquely specify the sequence of wins and losses.

However, if the bets on each throw are different, as shown in Figure 2, then knowing the score implies a knowledge of the sequence of wins and losses.

Since $|F_h|$ values in structure studies are inclined to be varied, much can be learned about their signs from knowing the density $\rho(x)$ at one or more points. For example,

$$\sum_{h=4\pi} \pm |F_h| = \frac{V}{8} [\rho(0) + \rho(1/2) + 2\rho(1/4)] - \frac{F_0}{2} \quad (13)$$

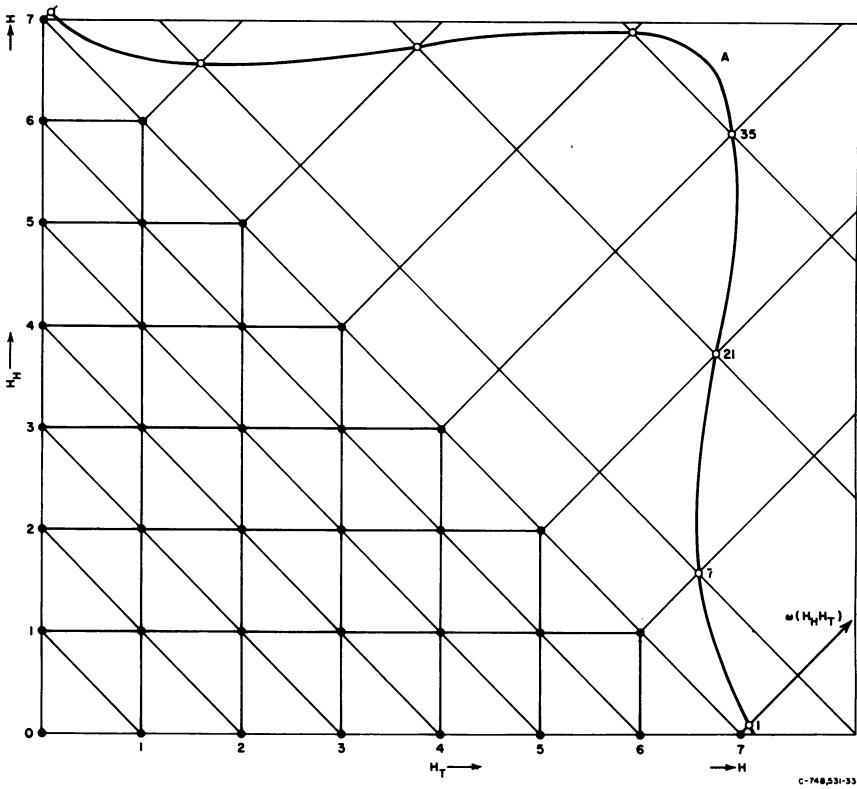


FIG. 1.—The straight line HH plotted from the equation $H_H + H_T = H$ for $H = 7$, representing the results in a penny-tossing game with equal bets on each toss. The dots on each diagonal line show the results after each toss, and the curve HAH shows a graph of the number of ways of attaining the final result, using equation (12). For example, there are 21 ways to win two times and lose five times in seven throws. Note that a knowledge of the score does not uniquely reveal the sequence of the game.

and

$$\sum_h \pm |F_h| = \frac{V}{8} [\rho(0) + \rho(1/2) - 2\rho(1/4)]. \tag{14}$$

$h = 4n + 2$

The values of $|F_h|$ shown in Figure 2 were taken from Sayre's discussion of his hypothetical structure. The same types of figures are also useful in studying Sayre's inner products in his squaring method of phase determination.

In order to solve for the most probable set of signs for the F values when no densities are known, it is necessary to assume a most probable density at some point and compute the compound probabilities of the combined densities at other points. These techniques will not be developed in this paper.

VII. *Resolution in Multiple Describees.*—In the above discussions little emphasis was placed on the fact that a crystal contains many identical unit cells, each one of which qualifies to be called a describee. This brings up the question, is the resolution improved by having a repeating pattern as compared to a single pattern? Physical optics teaches that the ultimate resolution to be expected when viewing a

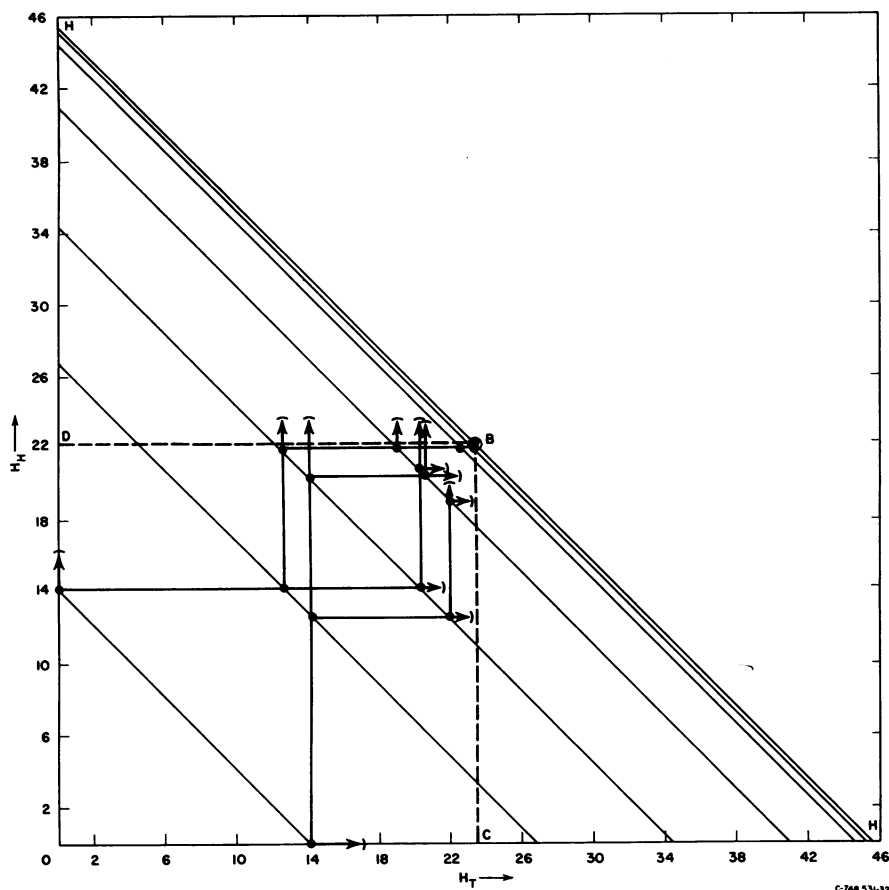


FIG. 2.—The results of tossing a penny seven times with a different bet for each throw. In this example (in contrast to that in Fig. 1) a knowledge of the final score does define the sequence of heads and tails. If the final terminus is at B , there is one and only one sequence of plays which can produce it. In arriving at B , one is guided by the fact that the dotted lines BC and BD cannot be crossed. This gives rise to dead ends, indicated by interrupted arrows. The data were taken from Sayre's¹⁵ hypothetical structure. All phases of F_h for $h = 4n$ are predicted, see eq. (13). (NOTE: In general, this determinism is maintained only if the first, second, third, etc., differences between bets are different.)

single pattern with radiation of wave length λ is $\lambda/2$; while experimental X-ray structure analysts commonly report accuracies in locating atoms to 0.01 Å and occasionally 0.003, using copper radiation with wave length $\lambda = 1.54$ Å. A crystal having mosaic blocks only 900 Å on an edge and unit cells of 3 Å, for example, has 300 unit cells on an edge or 2.7×10^7 unit cells in the volume. One might guess that the linear resolution might be $1.54/(2 \times 300) = 0.00256$ for this case, but this has not been proved.

However, the superior resolution in repeating patterns was implied previously (see section III) when the assumption was made that the descriptive capacity ω_d of the diffraction pattern is a function of $S_h = |F_h|/|F|_w$. The value of $|F|_w$, i.e., the weakest diffraction maximum, is influenced by the conditions of measurement of the integrated intensity, E ,

$$E_{hkl} = \frac{I_0 \lambda^3}{\omega} \left(\frac{e^2}{mc^2} \right)^2 \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} |F_{hkl}|^2 N^2 \Delta V, \quad (15)$$

where ΔV is the volume of the crystal contributing. The larger ΔV is, the greater and more reliable is E_{hkl} , and hence smaller $|F|_{\omega}$ are recorded, thus increasing all S_h terms. This can also be shown either by the methods outlined by McLachlan¹⁸ for resolution in diffraction patterns or by suggestions in the work of McLachlan and Christ.¹⁹

A neat way of demonstrating the combined information capacity of a multiple pattern is shown in Figure 3, *a*, *b*, and *c*. A page of 100 3-cent U.S. postage stamps is shown in Figure 3, *a*, taken on grainy film. An enlargement of a single one of this set is presented in Figure 3, *b*, to show the poor resolution. The negative of Figure 3, *a*, was placed on the traveling stage of a microscope, and a multiple exposure of 25 separate stamps out of the group of 100 was impressed on the same photomicrographic plate, each at 1/25 of the exposure time used for Figure 3, *b*. The result is shown in Figure 3, *c*. While Figure 3, *a*, might have a number of silver grains distributed between the 100 (or less) pictures to make a well-resolved picture, there are too few per picture. Figure 3, *c*, shows the combined effect of all the grains from 25 pictures influencing one picture. The details are better resolved. This is in accordance with the use of Poisson's law for predicting resolution as a function of silver-grain concentration. Computations indicate that the linear resolution should be proportional to the square root of the number of silver grains per unit area; and therefore Figure 3, *c*, should have five times the resolution of Figure 3, *b*.

The principles demonstrated by the postage-stamp experiment should prove to be very useful. If an electron micrograph of the face of a single crystal could be obtained showing the unit cells but not clearly enough to reveal the molecules or atoms, then the above procedure of combining the information of all the cells into one should result in an increased resolution of from tens to hundreds, depending upon the number of unit cells photographed on the crystal face and upon the accuracy of superposition.

VIII. *Conclusions.*—In conclusion, one may deduce from information theory that the X-ray data are usually sufficient for the solution of crystal structure. The solution of the problems of phase determination lies in the relationships between the magnitudes of the F values. Also, information theory (or description mechanics) points the way to extending the resolution of detail in electron micrographs of crystals.

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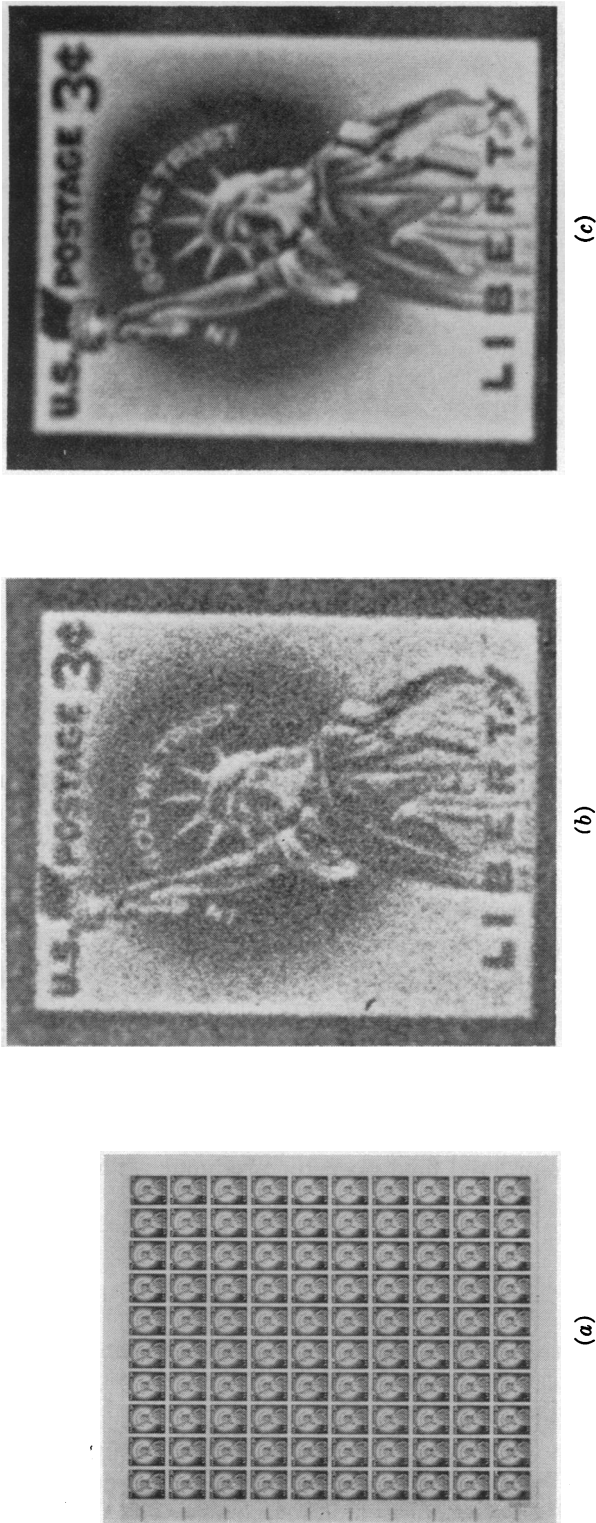


FIG. 3.—An example of the treatment of multiple describees: (a) a page of 100 U.S. 3¢ postage stamps taken on a coarse-grain film, Eastman Royal X-Pan; (b) an enlargement of one of the stamps from (a) using fine-grain paper to resolve the grain; and (c) a multiple exposure of 25 of the stamps from (a), each taken at $\frac{1}{25}$ the exposure of (b). Note the better resolution of the word “trust” and of the left hand holding the scroll.

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ON THE EUCLIDEAN STRUCTURE OF RELATIVISTIC FIELD THEORY

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The nature of physical experience is largely conditioned by the topology of space-time, with its indefinite Lorentz metric. It is somewhat remarkable, then, to find that a detailed correspondence can be established between relativistic quantum field theory and a mathematical image based on a four-dimensional Euclidean manifold. The situation can be characterized in the language of group theory, with physical quantities and states appearing as representations of the underlying Lorentz transformation group. It is well known that some representations of the Lorentz group can be obtained from the attached Euclidean group (the "unitary trick" of Weyl). What is being asserted is that *all* representations of physical interest can be obtained in this way.

The objects that convey this correspondence are the Green's functions of quantum field theory,¹ which contain all possible physical information. We consider a general Hermitian field, χ , which decomposes into a Bose-Einstein field ϕ , and a Fermi-Dirac field ψ . The Green's functions can be defined as vacuum-state expectation values of time-ordered field operator products. There are two types:

$$G_+(x_1 \dots x_p) = \langle (\chi(x_1) \dots \chi(x_p))_+ \rangle \epsilon_+(x_1 \dots x_p)$$

and

$$G_-(x_1 \dots x_p) = \langle (\chi(x_p) \dots \chi(x_1))_- \rangle \epsilon_-(x_p \dots x_1),$$

where positive or negative time ordering implies an assignment of multiplication order in accordance with the ascending sense of time, as read from right to left (+) or from left to right (-). The quantities ϵ_{\pm} are antisymmetrical functions of the time co-ordinates for the F.D. fields, which assume the value +1 when the time-ordered sense coincides with the written order. The connection between the two Green's functions is simply